



Hydrogen production from E85 fuel with ceria-based catalysts

Scott L. Swartz^{a,1}, Paul H. Matter^{a,*}, Gene B. Arkenberg^{a,1},
Franklin H. Holcomb^{b,2}, Nicholas M. Josefik^{b,2}

^a NexTech Materials, Ltd., 404 Enterprise Drive, Lewis Center, OH 43035, United States

^b The U.S. Army Engineer Research and Development Center, Construction Engineering Research Laboratory, ERDC-CERL, PO Box 9005, Champaign, IL 61826, United States

ARTICLE INFO

Article history:

Received 28 October 2008

Received in revised form 2 December 2008

Accepted 3 December 2008

Available online 7 December 2008

Keywords:

E85

Ethanol

Iso-octane

Steam reforming

Ceria

Rhodium

ABSTRACT

The use of renewable (crop-derived) fuels to produce hydrogen has considerable environmental advantages with respect to reducing net emissions of carbon dioxide into the atmosphere. Ethanol is an example of a renewable fuel from which hydrogen can be derived, and E85 is a commercially available ethanol-based fuel of increasing importance. The distributed production of hydrogen from E85 fuel is one potential way of assuring availability of hydrogen as PEM fuel cells are introduced into service. NexTech Materials is collaborating with the U.S. Army Construction Engineering Laboratory (CERL) on the development of a hydrogen reformation process for E85 fuel. This paper describes the technical status of E85 fuel reforming process development work using Rh/ceria catalysts. Reforming results are compared for steam reforming and oxidative steam reforming of ethanol (the primary constituent of E85 fuel), isooctane, ethanol/iso-octane fuel mixtures (as a surrogate to E85), and commercially available E85 fuel. Stable reforming of E85 at 800 °C and a space velocity of 58,000 scm³ g_{cat}⁻¹ h⁻¹ over a 200-h period is reported.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

As oil supplies dwindle, other sources of energy need to be developed to support the growing energy needs of the world. There is no single energy solution for the future, with coal, solar, wind, nuclear and fuel cells all having their place. The use of liquid fuels, such as ethanol, produced from renewable resources, is an attractive intermediate approach for energy production which reduces near-term reliance on fossil fuels, while alternative energy technologies are being established.

The U.S. military is in a unique position to support the demonstration of emerging renewable energy technologies. With a large number of military bases and installations throughout the world, there is opportunity for significant cost savings, as well as environmental stewardship. Further, highly trained personnel are available to support implementation of new energy technologies as they are introduced. The Army has been at the forefront of this trend. In 2005, the *Army Energy Strategy for Installations* was established [1,2], with the goal of: (1) eliminate/reduce energy and water usage in existing facilities, (2) increase energy efficiency in

renovation and new construction, (3) reduce dependency on fossil fuels, (4) conserve water resources, and (5) improve energy security.

Fuel cells offer a promising approach for achieving these goals. Fuel cells efficiently generate power from hydrogen or hydrocarbon fuels and greatly reduce emissions of pollutants. Fuel cells offer a near-term solution for conserving fossil fuels, and a long-term solution for generating power from renewable fuels. Of the various types, the proton exchange membrane (PEM) fuel cell operates at low temperature with pure hydrogen as fuel. PEM fuel cells are being developed for both stationary and transportation applications; the technology has matured to the point that systems are entering the demonstration phase of commercial acceptance. However, lack of availability of low-cost hydrogen limits the widespread use of PEM fuel cells.

Even before implementation of the *Army Energy Strategy for Installations*, the U.S. Army has been supporting its goals with a program aimed at demonstrating stationary fuel cells at military installations. In one such program, being led by the Army's Construction Engineering Research Laboratory (CERL), 93 PEM fuel cells have been installed at 56 different military sites. These fuel cells operate on hydrogen, which was either stored in cylinders or produced via on-site reformation of fossil fuels (natural gas or propane). A logical next step in development of fuel cell technology for stationary and transportation applications is the operation of fuel cells on hydrogen derived from renewable fuels. A partially renewable fuel of increasing importance is E85, which

* Corresponding author. Tel.: +1 614 842 6606; fax: +1 614 842 6607.

E-mail addresses: p.matter@nextechmaterials.com (P.H. Matter),

Franklin.H.Holcomb@erdcl.usace.army.mil (F.H. Holcomb).

¹ Tel.: +1 614 842 6606; fax: +1 614 842 6607.

² Tel.: +1 217 373 5864; fax: +1 217 373 6740.

is a blend of 85% ethanol (produced from corn) and 15% gasoline. Future commercial availability of E85 fuel is assured, given that this is the primary alternative fuel for “Flex-Fuel” vehicles that are being produced worldwide in ever increasing numbers. Although pure ethanol may be a more logical fuel choice for fuel cell systems, E85 was examined because of its widespread commercial availability.

To produce hydrogen from E85 fuel, the fuel must be reformed with steam and/or oxygen to produce a hydrogen-rich gas mixture that can be purified and collected. Reforming is a challenge because E85 fuel consists of two distinct types of hydrocarbons (ethanol and gasoline) and because the gasoline fraction contains sulfur that is a poison to most reforming catalysts. The demonstration of a suitable reforming catalyst and process is the first and most critical step toward demonstrating hydrogen production from E85 fuel.

In general, the level of difficulty for the reforming of hydrocarbon fuels increases with the complexity of the hydrocarbon fuel. Thus, ethanol with two carbon atoms in its structure is more difficult to reform than methane or methanol (both of which have one carbon atom in their structures). Gasoline is especially difficult to reform, given the multitude of different hydrocarbon species in gasoline and average carbon number of 7–8. It is particularly noteworthy that E85 is a fuel that contains two distinctly different components (ethanol and gasoline). Thus, a catalyst that works well for reforming of ethanol needs to work equally well for reforming of gasoline. The biggest challenge to designing catalysts for reforming of E85 fuel is the presence of sulfur in the fuel. This further limits the scope of available catalysts.

There has been a significant amount of reported work devoted to reforming of gasoline, diesel and logistic fuels, both for on-board fuel processing in automotive applications and for military fuel cell systems. Rhodium-based catalysts, and especially Rh/ceria catalysts, have been found to be extremely effective for reforming of these higher hydrocarbons with respect to obtaining high hydrogen yields without carbon deposition [3–7]. There also is a wide body of recent literature describing the steam reforming of ethanol for use in PEM fuel cell systems. Of the various catalysts evaluated, Rh/ceria catalysts were found to be extremely active for ethanol reforming, and more selective toward hydrogen [8–14], without formation of methane, ethylene and other undesired by-products of the ethanol decomposition reaction. Another potential advantage of Rh/ceria catalysts for steam reforming of ethanol is their high water-gas-shift activity, which leads to a reformed product gas with higher hydrogen and less carbon monoxide depending on temperature and steam content.

In this work, the activity, selectivity, and long-term stability of Rh/ceria catalysts for reforming of ethanol, iso-octane, mixtures of the two, and real E85 are examined. The affect of sulfur in the fuel on catalyst performance is also observed. Based on the demonstrated high performance of Rh/ceria catalysts for E85 steam reforming and oxidative steam reforming, the catalysts appear to be an excel-

lent material for distributed hydrogen production systems under development.

2. Experimental/materials and methods

2.1. Design and construction of liquid-fuel reforming reactor

Carefully designed fuel and steam delivery is necessary to demonstrate long-term catalyst performance when using liquid reactants under neat conditions. Oscillations in fuel to liquid ratio can cause carbon formation that ultimately leads to reactor failure. A liquid reforming test reactor was therefore designed and constructed for use in this research. The primary reactor components included: HPLC pumps for steady delivery of liquid reactants (water and fuel); mass flow controllers for delivering gaseous reactants (e.g., air); heated vaporization using NexTech's custom-built vaporizer design, a mixing chamber to dampen oscillations in vaporization and ensure even mixing of reactants; a packed bed catalyst chamber, a condensing system for removal of water and partially reacted condensable gases in the reformed product, and a gas chromatograph fitted with a thermal conductivity detector for product gas analysis. The reactor system allowed for testing catalysts under neat conditions (fuel and steam only) to simulate a real reforming system. The gas chromatograph (with helium carrier) was set up to detect the possible gaseous products, including: CO, CO₂, H₂, methane, ethane, and ethylene. The product analysis was further verified with a MKS Cirrus mass spectrometer.

2.2. Catalyst synthesis and characterization

Catalyst testing was performed using NexTech's 2-wt% Rh/ceria reforming catalyst, prepared by proprietary methods. The doped ceria catalyst support was prepared by a hydrothermal synthesis process that provides a thermally stable high surface area ceria-based mixed oxide support. Proprietary metal deposition and reduction methods were used to maximize rhodium dispersion and uniformity. The catalyst has a BET surface area of 64 m² g⁻¹, after deposition of rhodium. All catalysts were calcined at 800 °C prior to testing.

2.3. Catalyst testing

The catalyst was tested at various temperatures (700–800 °C), steam-to-carbon ratios (3–6), and oxygen-to-carbon ratios (0–0.25) with ethanol, ethanol/iso-octane, or E85 as the fuel. An outline of the test conditions reported in this study is shown in Table 1. The sulfur content of the commercial E85 was estimated based on sulfur exiting the reactor, detected by a mass spectrometer. Tests were carried out at steady-state over hundreds of hours to observe signs of catalyst deactivation (visible by breakthrough of unreformed hydrocarbons) or carbon formation (causing increased pressure drop and reactor failure). Space velocities were chosen to achieve

Table 1
Breakdown of long-term testing conditions for 2% Rh/ceria catalyst.

Fuel	T (°C)	SV (scm ³ g ⁻¹ h ⁻¹)	Steam/carbon ratio	O ₂ /carbon ratio	Sulfur content in fuel (ppmw)	Test duration (h)	Figure(s) showing results
Ethanol	700	20,000–50,000	3–5	0	0	100	1
Iso-octane	800	18,000–55,000	5–6	0.00–0.13	0	50	2
E85 surrogate	800	68,000–80,000	5–6	0.00–0.25	0	50	3–4
E85 surrogate	750–800	48,000	5	0	0	80	5
E85 surrogate	800	58,000	6	0	5	40	6
E85 surrogate	800	58,000	6	0	20	75	7
Commercial E85	800	58,000	6	0	~10	100	8
Commercial E85	800	48,000–58000	5–6	0.00–0.13	~10	125	9–10
Commercial E85	800	58,000	6	0	~10	200	11

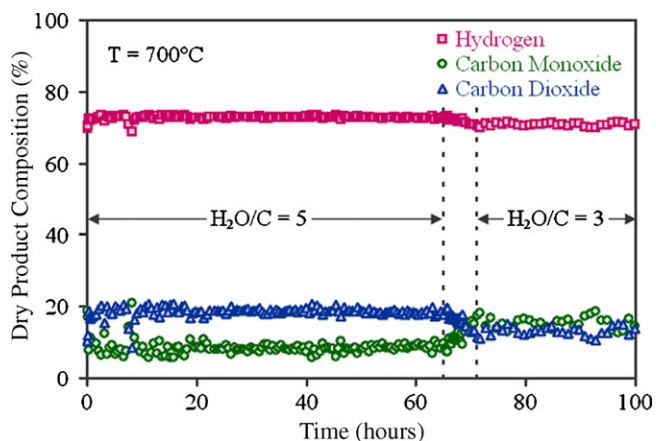


Fig. 1. Data obtained for steam reforming of ethanol at 700 °C, showing the effect of H₂O/C ratio on gas composition.

full fuel conversion of hydrocarbons, as the presence of unreformed hydrocarbons in the exhaust can lead to coke formation when the products are cooled down before analysis with the GC.

3. Results

3.1. Ethanol reforming

Several ethanol reforming tests were performed to assess the effects of reaction conditions, such as temperature, steam-to-carbon ratio, and oxygen-to-carbon ratio. Catalyst weight (0.5 g) and ethanol flow rate (0.088 cm³ min⁻¹ liquid or 34.0 scm³ min⁻¹ vapor) were held constant during the testing, with steam and air flows adjusted to achieve targeted oxidant (H₂O/C and O₂/C) ratios. Simulated air (20% O₂ in He) was used to introduce oxygen. Space velocities ranged from 20,000 to 50,000 scm³ g_{cat}⁻¹ h⁻¹ (depending on the H₂O/C and O₂/C ratios). The space velocity was adjusted so the only product gases observed were H₂, CO and CO₂. Methane was below the detectable limit of 0.2% for the TCD.

For ethanol reforming over Rh/ceria catalysts, the highest hydrogen yields are obtained by operating in the pure steam reforming mode (i.e., with no oxygen present). As shown in Fig. 1, stable steam reforming of ethanol was observed at 700 °C during 100 h of testing with H₂O/C ratios of 5/1 and 3/1. As expected from water-gas-shift equilibrium, higher steam content increased the yield of hydrogen and carbon dioxide. A number of further ethanol reforming tests also were conducted with oxygen being fed with steam over the catalyst (data not shown). No apparent benefit of oxygen with respect to either lowering operating temperature or increasing space velocity was observed for ethanol reforming.

3.2. Iso-octane reforming

The Rh/ceria catalyst also was used for reforming of iso-octane, which has a similar structure to gasoline without any sulfur contamination. Catalyst weight (0.5 g) and iso-octane flow rate (0.064 cm³ min⁻¹ liquid or 8.76 scm³ min⁻¹ vapor) were constant during testing, with steam and air flows adjusted to achieve targeted H₂O/C and O₂/C ratios. Space velocities ranged from 18,000 to 55,000 scm³ g_{cat}⁻¹ h⁻¹ (based on input gas flows). Data obtained in a 50-h iso-octane reforming test at 800 °C are shown in Fig. 2. In these tests, the primary product gases included H₂, CO and CO₂ (and He when oxygen was included as one of the reactants). Trace amounts of CH₄ also were detected (0.2–1.0%), its relative amount decreasing when oxygen was present and when the steam/carbon ratio was increased. Again stable reforming perfor-

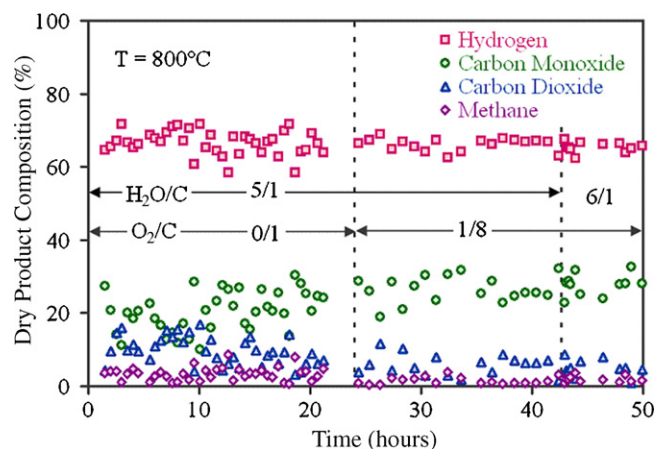


Fig. 2. Data for steam reforming of iso-octane at 800 °C, with varying H₂O/C and O₂/C ratios. Note that helium is present when O₂ is a reactant, but is not included in product gas composition for simplicity of interpretation.

mance was observed over 50 h of testing. The apparent stability of the catalyst in these tests suggested that the same Rh/ceria catalyst composition that was effective for reforming of ethanol also was effective for reforming of iso-octane. This provided confidence for testing work to proceed onto surrogate E85 fuels and ultimately to commercial grade E85 fuel.

3.3. Reforming of surrogate E85 fuel

A blend of 85 vol% ethanol and 15 vol% iso-octane was used as a sulfur-free surrogate to E85 fuel. Two tests were conducted with the Rh/ceria catalyst (0.5 g) and fuel flow rate of 0.0974 cm³ min⁻¹ liquid (33.8 scm³ min⁻¹ vapor). Complete conversion of the hydrocarbons was obtained at space velocities ranging from 68,000 to 80,000 scm³ g_{cat}⁻¹ h⁻¹. In the first test, effects of reactant composition (H₂O/C and O₂/C) were evaluated at 800 °C. For the first 25 h of this test, the H₂O/C ratio was 6/1 and the O₂/C ratio varied from 0 to 0.25 (see Fig. 3). For the second 25 h, the H₂O/C ratio was 5/1 and O₂/C varied from 0.06 to 0.25 (see Fig. 4). With these conditions, the catalyst provided stable performance, and the only product gases observed were H₂, CO, CO₂, and CH₄. The variation of oxygen levels had no noticeable effect on the hydrogen yield. Relatively high CO/CO₂ ratios were observed, higher than the ethanol product obtained under identical conditions. A second test was conducted with the catalyst operating in the pure steam reforming

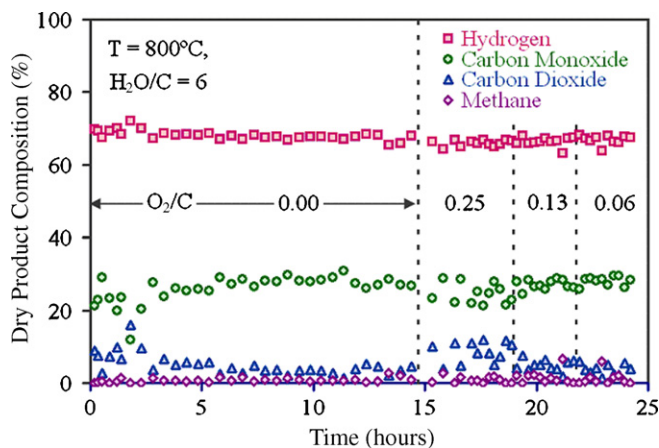


Fig. 3. Data obtained for reforming of sulfur-free surrogate E85 fuel at 800 °C with H₂O/C = 6/1 and various O₂/C ratios (helium is not shown for simplicity of interpretation).

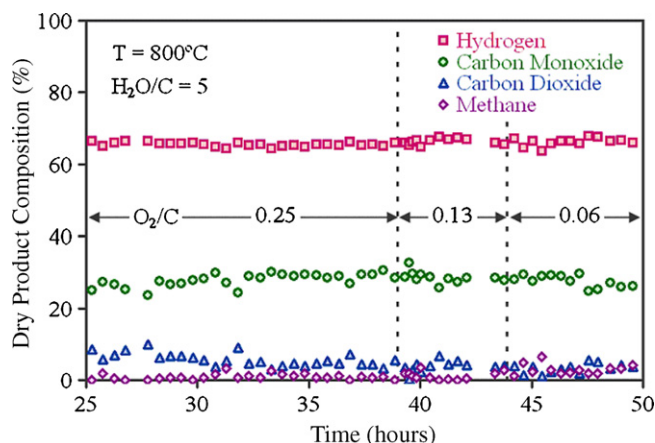


Fig. 4. Data obtained for reforming of sulfur-free surrogate E85 fuel at 800 °C with H₂O/C = 5/1 and various O₂/C ratios (helium is not shown for simplicity of interpretation).

mode (H₂O/C = 5) at temperatures of 800 and 750 °C (see Fig. 5). The catalyst provided stable reforming performance, also with a relatively high CO/CO₂ ratio and trace amounts of methane.

Steam reforming tests were conducted with a sulfur-containing surrogate to E85 fuel, by adding ethyl mercaptan (CH₃CH₂SH) to the ethanol/iso-octane fuel blend (5 and 20 ppm by weight sulfur). Two steam reforming tests were conducted, with catalyst weight (0.65 g), fuel flow rate (0.103 cm³ min⁻¹ liquid), and H₂O/C ratio (6/1) being held constant. In the first test (see Fig. 6), the steam reforming reaction was run for 20 h with sulfur-free surrogate fuel, and stable performance was achieved. Sulfur was then introduced into the fuel (5 ppmw), and the test continued for another 18 h. There was no apparent effect of 5-ppm sulfur on product gas composition. In the second test (see Fig. 7), steam reforming was initiated with 5 ppm sulfur for the first 5 h. The sulfur content of the fuel was then increased to 20 ppm and the test was run for an additional 70 h, with no observed effect of sulfur on product gas composition or catalyst stability. For both of these tests, the higher H₂O/C ratio and higher catalyst loading resulted in a significantly higher yield of CO₂ (which translates to increased H₂ yield).

3.4. Reforming of commercial E85 fuel

Finally, reforming tests were conducted with commercial E85 fuel purchased at a local gas station. Catalyst weight (0.65 g) and fuel flow rate (0.10 cm³ min⁻¹ liquid or 35 scm³ min⁻¹ vapor) were

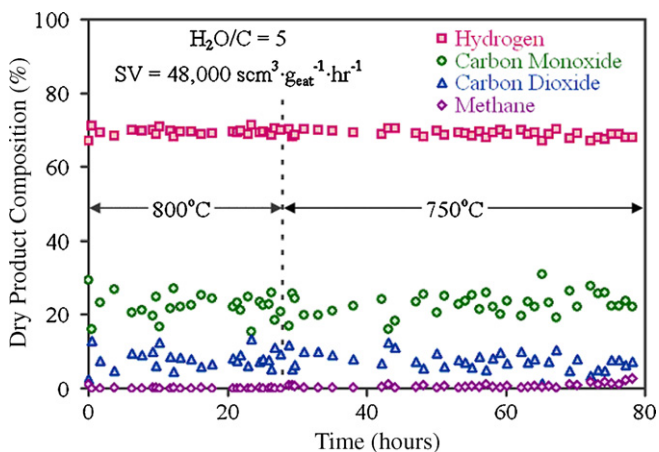


Fig. 5. Data obtained for steam reforming of sulfur-free surrogate E85 fuel at 800 and 750 °C with H₂O/C = 5.

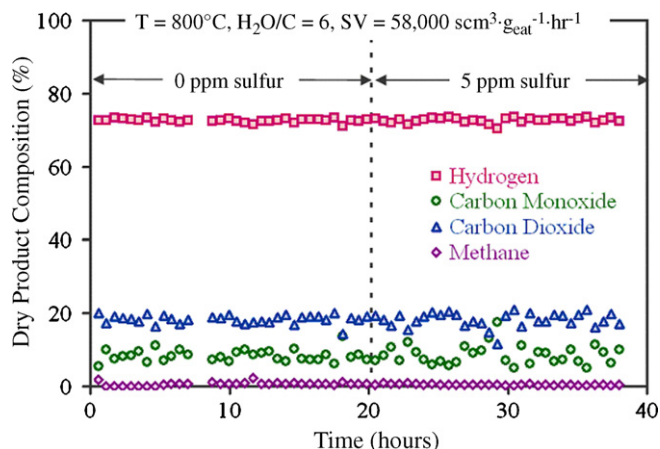


Fig. 6. Data obtained for steam reforming of surrogate E85 fuel (with 0 and 5 ppmw sulfur) at 800 °C with H₂O/C = 6.

held constant in these tests. In addition to gas chromatography, a mass spectrometer was used to provide a second means of product gas analysis (and to provide more accurate quantification of H₂ due to the low response of the TCD to H₂ in a helium carrier gas). A steam reforming test (H₂O/C = 6, T = 800 °C) was performed as a continuation of the above described test with sulfur-containing surrogate E85 fuel (see Fig. 8). Stable steam reforming on real E85 was achieved for an additional 100 h.

A second test was conducted with a fresh catalyst sample, starting out under the same steam reforming conditions (H₂O/C = 6, T = 800 °C), with both GC and MS methods used for product gas analysis (see Fig. 9). Stable performance and a good agreement of product gas compositions measured by GC and MS methods. During this test a measurable increase in methane from 0.2% to 1.8% was observed over the first 20 h, apparently due to loss in activity. After 27 h, the conditions were adjusted to oxidative steam reforming (H₂O/C = 5, O₂/C = 0.13), and the test was continued with stable reforming observed for an additional 100 h (see Fig. 10). The yields of H₂, CO and CO₂ were similar to those observed with steam reforming, and the concentration of methane remained stable for the remainder of the test.

A final long-term steam reforming test was performed at 800 °C with H₂O/C = 6 to confirm the stability of the catalyst in the absence of oxygen. The catalyst exhibited stable performance for 200 h

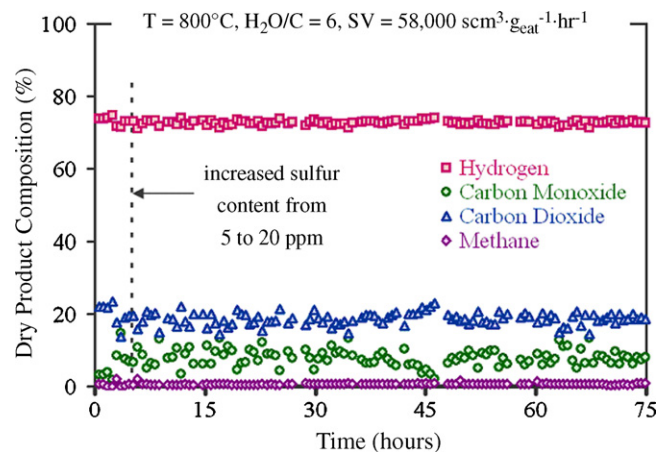


Fig. 7. Data obtained for steam reforming of surrogate E85 fuel (5 and 20 ppmw sulfur) at 800 °C with H₂O/C = 6.

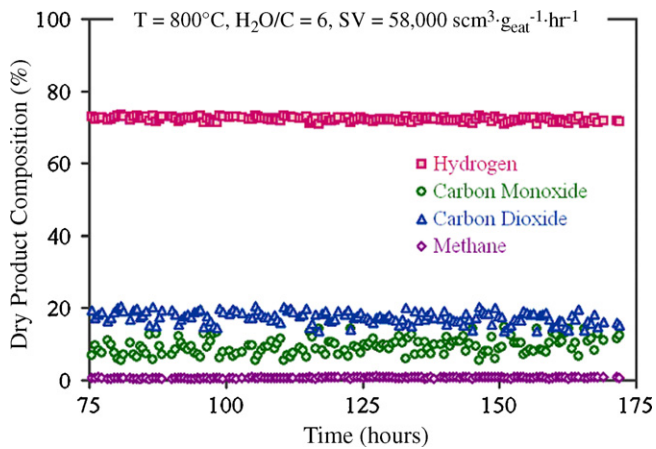


Fig. 8. Data obtained for steam reforming of commercial E85 fuel at 800 °C with $H_2O/C = 6$. Note that this test was initiated after 75 h of testing with sulfur-containing E85 surrogate fuel.

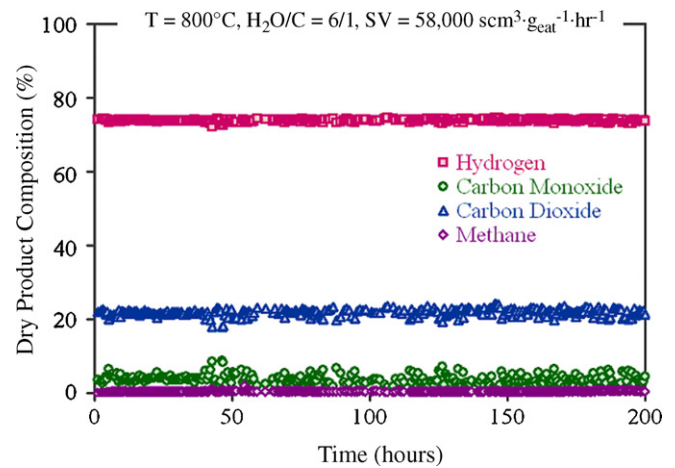


Fig. 11. Data obtained for steam reforming of commercial E85 fuel at 800 °C ($H_2O/C = 6$).

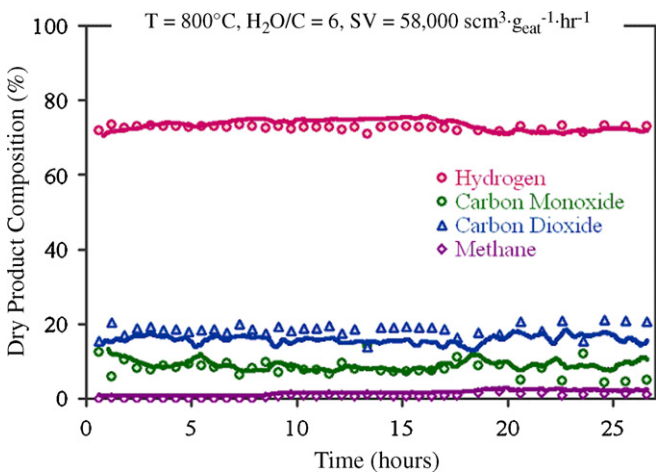


Fig. 9. Product gas analyses by gas chromatography (points) and mass spectrometry (lines) during steam reforming of commercial E85 fuel at 800 °C ($H_2O/C = 6$).

under steam reforming conditions, with a dry product gas composition for this test was 73.4% H_2 , 20.7% CO_2 , 5.3% CO , and 0.6% CH_4 (see Fig. 11). No measurable loss in activity could be observed for the duration of this test.

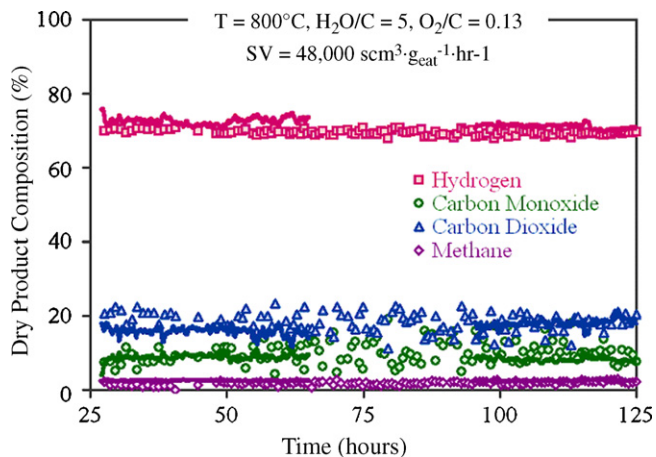


Fig. 10. Product gas analyses by GC (points) and MS (lines) during oxidative steam reforming of E85 fuel at 800 °C for $H_2O/C = 5$, and $O_2/C = 0.13$ (helium is not shown for simplicity of interpretation).

4. Discussion

The data demonstrates the remarkably good stability of Rh/ceria catalysts for steam and oxidative steam reforming of ethanol, iso-octane, and commercial E85 over hundreds of hours. Ethanol was the easiest fuel to reform of the three in terms of operating temperature and steam content required to demonstrate stability. The catalyst showed good stability at temperatures as low as 700 °C and 3/1 steam to carbon ratios. However, ethanol is already partially oxidized, and stoichiometrically less steam per carbon atom is required to reform ethanol. For fuels containing higher hydrocarbons, carbon deposition in the reactor entrance and exit were most often the cause of failed tests. Increasing the steam content and reformer temperature reduced the risk of carbon deposition and allowed tests to run for hundreds of hours without degradation. Iso-octane and E85 required similar operating conditions to prevent reactor failure, despite the fact that E85 contains mostly ethanol. The reforming catalyst performed well for both fuels at temperatures of 800 °C and 5/1 steam to carbon ratios. Future development should focus on reactor tubing and components that do not catalyze carbon precipitation, unlike the stainless steel components used in this work. This could possibly allow steam to carbon ratios to be lowered further, which would reduce system efficiencies associated with water vaporization.

In terms of catalyst loading, more catalyst (lower space velocity) was required to completely convert iso-octane and E85 compared to ethanol. While only 0.5 g of catalyst was required to obtain equilibrium product compositions for ethanol reforming, higher amounts of methane and high CO/CO_2 ratios were observed for iso-octane reforming under the same conditions. At slightly higher catalyst loading (0.65 g) complete conversion of methane was observed, and CO/CO_2 ratios were more similar to the values obtained with ethanol.

A very important result of the testing was that addition of sulfur did not adversely affect catalyst performance or long-term stability. No change in product composition was observed even upon introduction of up to the equivalent of 20 ppmw sulfur to the fuel, except for the presence of H_2S in the exhaust. Further, no degradation was observed in multiple tests lasting longer than 100 h for reforming of E85 surrogate containing 20 ppmw sulfur, and commercial E85. In previous steam reforming studies, the presence of sulfur in the fuel stream typically has a significant effect of steam reforming activity, even for precious metal-based catalysts [7,15,16]. It is believed that the higher temperatures and steam contents of the current test could be playing a role in sulfur tolerance of the catalysts.

5. Conclusions

NexTech Materials initiated development of a reforming process for E85 fuel as a first step toward building a hydrogen production system. The primary focus of this work was to demonstrate performance and longevity of ceria-supported rhodium catalysts for the reforming of E85 fuel. Significant results are summarized by the following conclusions:

- 2% Rh/ceria was found to be an excellent catalyst for reforming of E85 fuel due to its high activity and stability at high space velocity, and limited selectivity toward methane formation.
- The ceria-based catalyst was highly active for reforming of both ethanol and iso-octane (the two constituents of E85 fuel), and also for reforming of a surrogate fuel mixture of ethanol and iso-octane. Based on the ease of reforming ethanol compared to iso-octane (good stability at lower temperatures and lower steam to carbon), pure ethanol would be a better choice than E85 for reforming systems.
- The addition of sulfur (in the form of ethyl mercaptan) had no observable effect on reformer activity or stability at sulfur contents of up to 20 ppmw for the target space velocities.
- The ceria-based catalyst was active and stable for steam reforming of commercial E85 fuel ($H_2O/C=6$) at $800^\circ C$ during 200 h of testing. The reformed syngas contains approximately 73% hydrogen on a dry basis under these conditions.
- The ceria-based catalyst was active and stable for oxidative steam reforming ($H_2O/C=5$, $O_2/C=0.13$) at $800^\circ C$ during 100 h

of testing. The dry reformed syngas contains approximately 70% hydrogen under these conditions.

Acknowledgement

This work was funded by the U.S. Army under Contract No. W9132T-07-C-0005.

References

- [1] Department of the Army, "Army Energy Strategy for Installations", July 2005, http://army-energy.hqda.pentagon.mil/docs/draft_strategy.pdf.
- [2] Department of the Army "Army Energy and Water Campaign Plan for Installations", August 2006, http://army-energy.hqda.pentagon.mil/docs/campaign_plan_01_08_06.pdf.
- [3] K. Polychronopoulou, J.L.G. Fierro, A.M. Efstathiou, *J. Catal.* 228 (2004) 417.
- [4] R.B. Biniwale, N.K.M. Ichikawa, *Catal. Lett.* 100 (2005) 17.
- [5] K.A. Williams, L.D. Schmidt, *Appl. Catal. A: Gen.* 299 (2006) 30.
- [6] B.J. Dreyer, I.C. Lee, J.J. Krummenacher, L.D. Schmidt, *Appl. Catal. A: Gen.* 307 (2006) 184.
- [7] J.J. Strohm, J. Zheng, C. Song, *J. Catal.* 238 (2006) 309.
- [8] E.C. Wanat, Venkataraman, L.D. Schmidt, *Appl. Catal. A: Gen.* 276 (2004) 155.
- [9] G.A. Deluga, J.R. Salge, L.D. Schmidt, X.E. Verykios, *Science* 303 (2004) 993.
- [10] J.R. Salge, G.A. Deluga, L.D. Schmidt, *J. Catal.* 235 (2005) 69.
- [11] A. Haryanto, S. Fernando, N. Murali, S. Adhikari, *Energy Fuels* 19 (2005) 2098.
- [12] J. Kugai, S. Velu, S. Song, *Catal. Lett.* 101 (2005) 255.
- [13] J. Kugai, S. Velu, S. Song, M.H. Engelhard, M.H. Chin, *J. Catal.* 238 (2006) 430.
- [14] H.S. Roh, Y. Wang, D.L. King, A. Platan, Y.H. Chin, *Catal. Lett.* 108 (2006) 15.
- [15] A.-M. Azad, M.J. Duran, *Appl. Catal. A: Gen.* 330 (2007) 77.
- [16] A.-M. Azad, M.J. Duran, A.K. McCoy, M.A. Abraham, *Appl. Catal. A: Gen.* 332 (2007) 225.